Interaction of Carbon Monoxide with Fe(001)

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New insight into the bonding of carbon monoxide with transition-metal surfaces is provided by spin-polarized photoemission studies of CO on Fe(001). The interaction of the molecular 5σ levels with the substrate d bands is found to be very weak for both tilted and vertical CO species. The former shows clear evidence for a π-d-band interaction with discrete spin-polarized features in the occupied d band; the latter shows only small changes. Inverse photoemission studies (non-spin-polarized) indicate that the unoccupied 2π level is closer to the Fermi level for the tilted CO species.

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The catalytic properties of transition-metal surfaces have motivated much of the surface science research into the chemisorption of atoms and molecules.[1] Foremost has been the study of the interaction of carbon monoxide, which has become the model system for understanding nondissociative molecular chemisorption. However, despite numerous studies over many years, there still exists considerable debate over the importance of the various orbital interactions. The CO molecule usually bonds vertically to the surface through the carbon atom. However, there are strong-chemisorption (e.g., nickel) and weak-chemisorption (e.g., copper) limits, and cases of tilted and lying down molecules are also reported.[2]

The interaction of carbon monoxide with Fe(001) has attracted considerable interest,[3–8] particularly with the observation of an anomalously low stretching mode in electron energy-loss experiments.[3] The room-temperature adsorption state is found[4] to be tilted 55° from the normal along the [100] azimuth and further to be situated in the fourfold hollow site, as are oxygen and sulfur. At approximately 440 K (Ref. 5) this tilted species is found to partly desorb and partly dissociate leading to oxygen and carbon atoms randomly occupying fourfold hollow sites.[6] It is thought[7] that this molecular species is a precursor to dissociation and important in the catalytic behavior of iron. At low temperatures (150 K) a second species adsorbs along with the tilted species. This second low-temperature species has stretching frequencies[3] typical of a vertical CO molecule in a top or bridge site although the exact site is unknown. However, these two CO species allow comparisons between a strong- and a weak-chemisorption system.

Several theoretical models have been suggested to describe the chemisorption of molecular CO. The Blyholder model,[9] which has its origin in transition-metal carbonyl chemistry, proposes that the bonding mechanism involves electron donation from the CO 5σ orbital into the unoccupied metallic d orbitals accompanied by back donation from the occupied d orbitals into the empty CO 2π orbital. An alternative picture,[10] which has developed out of the Anderson-Newns model of chemisorption,[11] involves an increased participation of the substrate s,p continuum and proposes that the hybridization of the localized adsorbate valence orbitals with substrate s, p, and d bands leads to resonances whose width reflects the strength of the adsorbate-substrate coupling. For CO adsorption it is suggested[10] that an unoccupied 2π resonance state may extend below the Fermi level allowing backbonding into the resonance.

In this Letter we present the results of an angle-resolved spin-polarized photoemission study of the interaction of the different CO species with the Fe(001) surface. Recently,[12] it has been shown that oxygen and sulfur overlayers on Fe(001) show a large exchange splitting in the adsorbate levels, a direct reflection of the interaction of the substrate d bands with the adsorbate p levels. In addition, new spin-polarized states (both minority and majority) were observed within the substrate valence bands. The ionization potential of the CO 5σ orbital is similar to that for the $2p$ level of atomic oxygen and therefore a measurement of the polarization of the molecular orbital should provide further insight into the chemisorption mechanism. Symmetry restricts the 5σ orbital to interact with the substrate $d\sigma$ levels (bulk e_g symmetry). The unoccupied e_g states are almost entirely minority in character and therefore any bonding determined solely by interaction with them should result in a strong polarization effect. Changes in the occupied valence bands on the other hand, should reflect the interaction of the 2π level with the d bands. In addition, inverse-photoemission measurements are used to determine the position of the empty states above the Fermi level and allow a more complete view of the interaction.

The spin-polarized photoemission experiments reported here were carried out using an instrument which will be described in detail elsewhere.[13] Briefly, spin detection is achieved with a compact low-energy spin detector[14] and uses light provided by the U5 vacuum-ultraviolet undulator at the National Synchrotron Light Source.[15] The angular resolution of the electron spectrometer was $\pm 1.5°$ and the combined photon and analyzer energy resolution was 0.35 eV. The Fe(001) crystal was manufactured in the form of a picture frame with each leg along a ⟨100⟩ direction and magnetized using a coil wound around one leg. In a separate experimental chamber, photons in the range 10–30 eV emitted in the inverse-photoemission process are detected with a grating spectrograph described in detail elsewhere.[16] At the incident electron beam energy used in the present study, 20.85 eV, the overall resolution was approximately 0.47 eV. In both experiments low-energy electron diffraction and Auger electron spectroscopy were used to monitor the surface order and cleanliness, respectively.

The clean sample was prepared by cycles of argon bombardment and annealing.[17] The tilted CO species was generally produced by dosing at or just below room temperature, a 0.5-L [1 L (langmuir) $=10^{-6}$ Torr sec] exposure giving a $c(2\times2)$ overlayer. The same result could also be achieved by dosing <0.2-L CO at 150 K. A 2-L CO exposure at 150 K gives rise to the vertical CO species in addition to the tilted, in agreement with previous work.[3,5] Photoemission[8] has previously identified the adsorbate-induced features below the valence band. Our results (not shown) are in general agreement. In studies with mixed adsorption, the vertical and tilted species can be separated by appropriate choice of experimental conditions. For instance, at normal emission and a photon energy of 46 eV, the vertical-CO–derived features are approximately 5 times more intense than the tilted-CO features.

The 4σ, 1π, and 5σ levels for the vertical species are found at 10.9-, 8.1-, and 7.1-eV binding energy, respectively, the ordering of the 1π and 5σ levels being determined by making use of the polarization of the light from the storage ring. The 5σ level has moved towards the 1π and 4σ levels in a manner consistent with a weakly chemisorbed system. The tilted CO species represents a strongly interacting system as indicated by the stretched CO bond.[3,7] In the photoemission spectra, the 5σ and 1π levels could not be resolved due to the reduced symmetry and the presence of four domains. The reduced symmetry leads to a hybridization of the σ and π levels such that the gas-phase notation is no longer strictly appropriate. However, peaks occur at approximately 8.0- and 12.0-eV binding energy with the former representing emission from the "1π,5σ" levels and the latter emission from the "4σ" level. It has been suggested[8] that the deeper binding energy of the "4σ" level (compared to that for vertical CO) indicates involvement of this level in the bonding as final-state effects would be expected to move this level to lower binding energy. In the present study no exchange splitting (<0.1 eV) was observed in any of the adsorbate levels below the valence band. Figure 1 shows the results of a spin-polarized study of the 1π and 5σ levels for the vertical species. A similar result was obtained for the $c(2\times2)$ tilted species with several points being sampled across the surface Brillouin zone. The dissociation of the tilted species at room temperature was characterized by a decrease in the intensity of the molecular adsorbate levels, including peaks

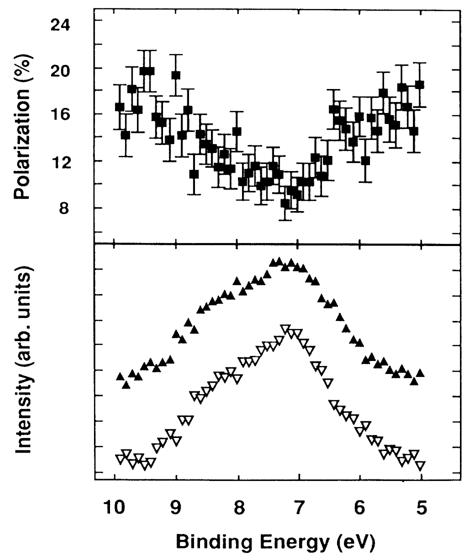

FIG. 1. Normal-emission spin-polarized photoemission spectra for the 1π,5σ CO levels taken at 46-eV photon energy, at an angle of incidence of 70°, and at 150 K, for Fe(001)+2-L CO. The polarization (■), minority (▽), and majority (▲) spectra are shown.

observed in the valence band, and the growth of a peak at 6.25-eV binding energy. This new peak, probably associated with atomic oxygen, was found to be highly polarized as in the case of an oxygen overlayer.[12]

Figure 2 shows the spin-polarized valence-band spectra for clean Fe(001) and with the tilted CO species. The minority feature at 2.4-eV binding energy in the clean spectra has been shown[18] to be a surface resonance and is quenched by small amounts of surface contamination. The new minority feature at 1.7-eV binding energy is clearly due to the presence of CO as is the majority feature at 2.3 eV. The CO-derived features are relatively strong at this photon energy ($h\nu=52$ eV) due to a low d-band cross section. The substrate s,p band, however, is found to be relatively intense at these same energies suggesting the possibility that the appreciable intensity of the CO peaks reflect the presence of a substrate p component in these levels. It should also be noted that these peaks are not necessarily exchange split but may well represent interaction with states of different symmetry. The effect of adsorption on the surface magnetism was monitored by following changes in the polarization of the Fe $3p$ core level. Surface sensitivity was maximized by choosing kinetic energies (~45 eV) close to the escape minimum ($\lambda\sim5$ Å). Since spin-polarized adsorbate-induced features are observed, the tilted CO has evidently not destroyed the surface magnetism, which is consistent with our observation of only a small decrease in the polarization of the Fe $3p$ level.

No new features are observed in the spectra shown in Fig. 2(b) with subsequent adsorption of the vertical

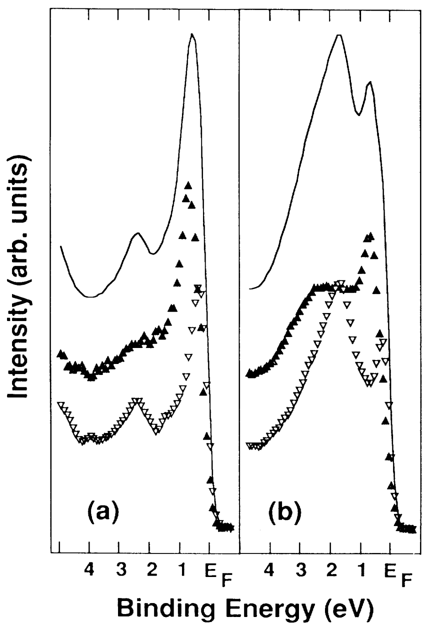

FIG. 2. Room-temperature normal-emission spin-polarized photoemission spectra taken at a photon energy of 52 eV and an angle of incidence $\phi_i = 70°$. The majority (▲), minority (▽), and spin-integrated (line) spectra are shown for (a) clean Fe(001) and (b) Fe(001)+0.5-L CO.

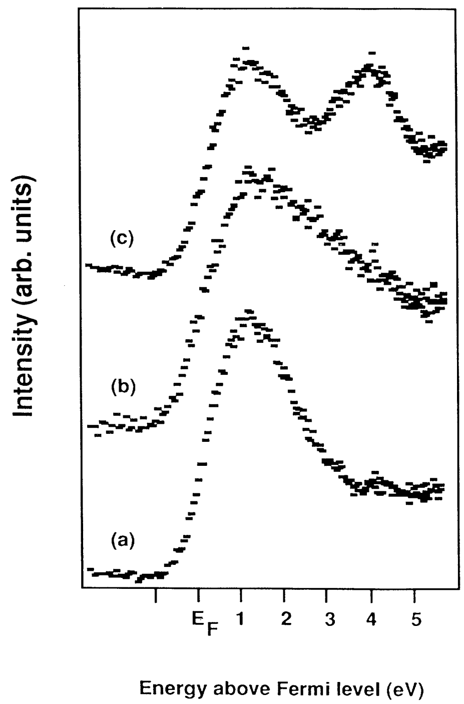

FIG. 3. Inverse-photoemission spectra, with an incident electron energy of 20.85 eV and angle of incidence of 45°, for (a) clean Fe(001) at 300 K, (b) Fe(001)+0.5-L CO at 300 K, and (c) Fe(001)+2-L CO at 150 K.

species. Similar experiments using *s*-polarized light, which should preferentially excite the 2π states for the vertical species, show only changes in the intensities of the spin-resolved *d* bands. These changes include a slight decrease in the substrate minority peak at the Fermi level and a small but significant increase in the intensity of the majority spectrum at approximately 0.75-eV binding energy. The polarization of the Fe $3p$ core level was essentially unchanged from that found with the tilted phase.

As noted earlier, most models suggest that for a vertical adsorption geometry changes in the occupied *d* bands will reflect back donation into the molecular 2π level. For the tilted phase with reduced symmetry and consequent σ-π hybridization the situation is slightly more complicated. However, it is clearly of interest to determine the position of the unoccupied "2π" level for the two adsorbate geometries. Inverse-photoemission spectra, taken at 45° angle of incidence, are shown in Fig. 3. The clean spectrum, Fig. 3(a), shows the empty *d* bands just above the Fermi level. Adsorption of the vertical CO species, Fig. 3(c), gives rise to a peak at approximately 4.0 eV above the Fermi level which we associate with the adsorbate 2π level. The more strongly bound or tilted CO species does not produce a clearly resolved peak, Fig. 3(b), but a difference spectrum indicates an adsorbate-induced feature at approximately 3.3 eV above the Fermi level. Desorption of the CO species is accompanied by a decrease in the intensity of these features. No changes were observed in the *d* bands.

Experimentally, CO chemisorption has been investigated with both photoemission[2] and inverse photoemission.[19,20] Although a considerable amount has been learned from such studies it has not always been possible to unravel initial-state effects, due to bonding, from final-state effects, due to the excited nature of the spectroscopies. As a consequence, the exact nature of the interactions are still a point of debate. As in the present study, photoemission experiments[2] show that the 5σ CO level is pulled to higher binding energies as compared to the gas-phase values. This is generally thought to reflect the bonding of this level to substrate bands. However, a similar result can also be obtained through a lengthening of the CO bond reflecting an interaction of the antibonding 2π level alone.[21] Bagus, Neli, and Bauschlicher[22] have further proposed that electrostatic shifts might be responsible for this increased binding energy of the 5σ level. The present spin-resolved study should allow the direct observation of any interaction of the 5σ level with the polarized substrate *d* bands. The clear lack of any discernible polarization for either CO species would therefore suggest that interaction with these bands is very weak if at all. *This has important implications for chemisorption models, particularly those involving substantial 5σ–d-band interactions.*

As regards the involvement of the 2π level in bonding to the valence bands, results have often been difficult to interpret. Only in the case of the (2×1) $p2mg$ CO structure on Ni(110)[23] has good evidence been obtained for dispersing CO-derived features in the valence band indicative of a more direct 2π–d-band interaction than suggested by the resonance models. Contrary to the expectations of a simple Blyholder model[9] inverse-photoemission experiments[19,20] have shown that peaks associated with the unoccupied 2π orbital move closer to the Fermi level as the substrate-CO interaction becomes stronger, an observation also made in the present study. Inclusion of the s,p-band interaction through the resonance model[10] can retrieve the situation. However, it has been argued[20] that since the magnitude of final-state effects are not known it is difficult to separate the various models. The 0.7-eV shift in this work can also be explained purely in terms of the increased CO bond length.[24] However, that probably represents an oversimplification. The results of the present study clearly indicate that in the case of the strongly chemisorbed tilted species a significant interaction with the substrate d bands occurs via the molecular "π" levels, with well defined new peaks emerging in the occupied valence bands. This interaction will result in a lowering of the stretch frequency and ultimate dissociation of the molecule. For the weakly bound vertical species, on the other hand, no well defined peaks pinpointing the role of the 2π level are observed. However, changes in the substrate d bands, with an increase in the intensity of one band and a decrease in the intensity of another band, indicate that such an interaction probably does occur. Final-state scattering in the overlayer would lead to a reduction in intensity of both the minority and majority bands.

In summary, our spin-polarized photoemission study of this carbon monoxide chemisorption system suggests that the principal interaction with the substrate d bands occurs via the unoccupied molecular 2π level.

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